US009252315B2

(12) **United States Patent**
Jones-Albertus et al.

(10) **Patent No.: US 9,252,315 B2**
(45) **Date of Patent: Feb. 2, 2016**

(54) **LATTICE MATCHABLE ALLOY FOR SOLAR CELLS**

(71) Applicant: **SOLAR JUNCTION CORPORATION**, San Jose, CA (US)

(72) Inventors: **Rebecca Elizabeth Jones-Albertus**, Washington, DC (US); **Homan Bernard Yuen**, Santa Clara, CA (US); **Ting Liu**, San Jose, CA (US); **Pranob Misra**, Santa Clara, CA (US)

(73) Assignee: **Solar Junction Corporation**, San Jose, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/678,737**

(22) Filed: **Apr. 3, 2015**

(65) **Prior Publication Data**

US 2015/0214412 A1 Jul. 30, 2015

Related U.S. Application Data

(60) Continuation of application No. 14/597,621, filed on Jan. 15, 2015, which is a continuation of application No. 14/512,224, filed on Oct. 10, 2014, now Pat. No. 9,018,522, which is a continuation of application No. 13/739,989, filed on Jan. 11, 2013, now Pat. No. 8,912,433, which is a division of application No. 12/749,076, filed on Mar. 29, 2010, now abandoned.

(51) **Int. Cl.**
H01L 31/00 (2006.01)
H01L 31/0735 (2012.01)
(Continued)

(52) **U.S. Cl.**
CPC ***H01L 31/0735*** (2013.01); ***C22C 28/00*** (2013.01); ***C22C 30/00*** (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC H01L 31/03042; H01L 31/03048; H01L 31/03046
USPC 136/255, 262
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,404,421	A	9/1983	Fraas
4,881,979	A	11/1989	Lewis

(Continued)

FOREIGN PATENT DOCUMENTS

JP	63100781	5/1988
JP	06061513	3/1994

(Continued)

OTHER PUBLICATIONS

Bank, et al., "Molecular-beam epitaxy growth of low-threshold cw GainNAsSb lasers at 1.5 μm," J. Vac. Sci. Technol. B 23(3), May/Jun. 2005, pp. 1337-1340.

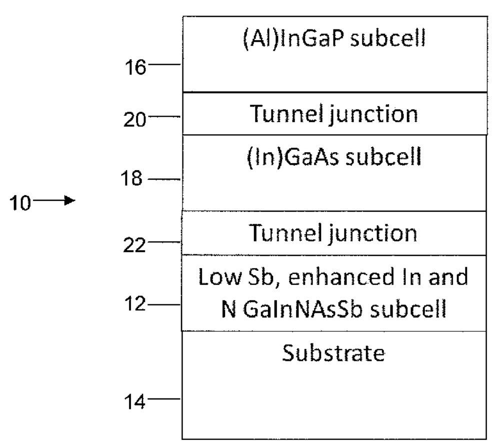
(Continued)

Primary Examiner — James Lin
Assistant Examiner — Dujuan Horton

(57) **ABSTRACT**

An alloy composition for a subcell of a solar cell is provided that has a bandgap of at least 0.9 eV, namely, $Ga_{1-x}In_xN_yAs_{1-y-z}Sb_z$ with a low antimony (Sb) content and with enhanced indium (In) content and enhanced nitrogen (N) content, achieving substantial lattice matching to GaAs and Ge substrates and providing both high short circuit currents and high open circuit voltages in GaInNAsSb subcells for multijunction solar cells. The composition ranges for $Ga_{1-x}In_xN_yAs_{1-y-z}Sb_z$ are $0.07 \leq x \leq 0.18$, $0.025 \leq y \leq 0.04$ and $0.001 \leq z \leq 0.03$.

9 Claims, 5 Drawing Sheets



(51) **Int. Cl.**

C22C 28/00	(2006.01)
H01L 31/18	(2006.01)
H01L 31/0304	(2006.01)
H01L 31/078	(2012.01)
H01L 31/0725	(2012.01)
C22C 30/00	(2006.01)

(52) **U.S. Cl.**

CPC ***H01L31/0304*** (2013.01); ***H01L 31/03048*** (2013.01); ***H01L 31/078*** (2013.01); ***H01L 31/0725*** (2013.01); ***H01L 31/1848*** (2013.01); *Y02E 10/544* (2013.01); *Y10T 428/12* (2015.01)

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,935,384	A	6/1990	Wanlass
5,009,719	A	4/1991	Yoshida
5,016,562	A	5/1991	Madan et al.
5,166,761	A	11/1992	Olson et al.
5,223,043	A	6/1993	Olson et al.
5,316,593	A	5/1994	Olson et al.
5,342,453	A	8/1994	Olson et al.
5,376,185	A	12/1994	Wanlass
5,405,453	A	4/1995	Ho et al.
5,689,123	A	11/1997	Major et al.
5,800,630	A	9/1998	Vilela et al.
5,911,839	A	6/1999	Tsai et al.
5,935,345	A	8/1999	Kuznicki
5,944,913	A	8/1999	Hou et al.
6,150,603	A	11/2000	Karam et al.
6,252,287	B1	6/2001	Kurtz et al.
6,281,426	B1	8/2001	Olson et al.
6,340,788	B1	1/2002	King et al.
6,504,091	B2	1/2003	Hisamatsu et al.
6,617,618	B2	9/2003	Sato
6,660,928	B1	12/2003	Patton et al.
6,756,325	B2	6/2004	Bour et al.
6,764,926	B2	7/2004	Takeuchi et al.
6,765,238	B2	7/2004	Chang et al.
6,787,385	B2	9/2004	Barber et al.
6,815,736	B2	11/2004	Mascarenhas
6,951,819	B2	10/2005	Iles et al.
7,071,407	B2	7/2006	Faterni et al.
7,119,271	B2	10/2006	King et al.
7,122,733	B2	10/2006	Narayanan et al.
7,122,734	B2	10/2006	Fetzer et al.
7,123,638	B2	10/2006	Leary et al.
7,126,052	B2	10/2006	Fetzer et al.
7,255,746	B2	8/2007	Johnson et al.
7,279,732	B2	10/2007	Meng et al.
7,709,287	B2	5/2010	Fatemi et al.
7,727,795	B2	6/2010	Stan et al.
7,807,921	B2	10/2010	Fetzer et al.
7,842,881	B2	11/2010	Comfeld et al.
8,067,687	B2	11/2011	Wanlass
8,575,473	B2	11/2013	Jones et al.
2002/0000546	A1	1/2002	Sato
2002/0195137	A1	12/2002	King et al.
2003/0070707	A1	4/2003	King et al.
2003/0145884	A1	8/2003	King et al.
2004/0045598	A1	3/2004	Narayanan et al.
2004/0130002	A1	7/2004	Weeks et al.
2004/0200523	A1	10/2004	King et al.
2005/0155641	A1	7/2005	Fafard
2005/0274409	A1	12/2005	Fetzer et al.
2006/0144435	A1	7/2006	Wanlass
2006/0162768	A1	7/2006	Wanlass et al.
2007/0034853	A1	2/2007	Robbins et al.
2007/0131275	A1	6/2007	Kinsey et al.
2007/0227588	A1	10/2007	Gossard et al.
2008/0035939	A1	2/2008	Puetz et al.
2008/0149173	A1	6/2008	Sharps
2008/0245400	A1	10/2008	Li
2008/0257405	A1	10/2008	Sharps
2009/0001412	A1	1/2009	Nagai et al.
2009/0014061	A1	1/2009	Harris et al.
2009/0057721	A1	3/2009	Miura et al.
2009/0078310	A1	3/2009	Stan et al.
2009/0145476	A1	6/2009	Fetzer et al.
2009/0155952	A1	6/2009	Stan et al.
2009/0229659	A1	9/2009	Wanlass et al.
2009/0255575	A1	10/2009	Tischler
2009/0255576	A1	10/2009	Tischler
2009/0272438	A1	11/2009	Cornfeld
2009/0288703	A1	11/2009	Stan et al.
2010/0087028	A1	4/2010	Porthouse et al.
2010/0096001	A1	4/2010	Sivananthan et al.
2010/0180936	A1	7/2010	Kim
2010/0218819	A1	9/2010	Farmer et al.
2010/0282305	A1	11/2010	Sharps et al.
2010/0282306	A1	11/2010	Sharps et al.
2010/0319764	A1	12/2010	Wiemer et al.
2011/0023958	A1	2/2011	Masson et al.
2011/0114163	A1	5/2011	Wiemer et al.
2011/0210313	A1	9/2011	Fuji et al.
2011/0232730	A1	9/2011	Jones et al.
2011/0303268	A1	12/2011	Tan et al.
2012/0031478	A1	2/2012	Boisvert et al.
2012/0103403	A1	5/2012	Misra et al.
2012/0211071	A1	8/2012	Newman et al.
2012/0216858	A1	8/2012	Jones-Albertus et al.
2012/0216862	A1	8/2012	Abou-Kandil et al.
2012/0227797	A1	9/2012	Stan et al.
2012/0285526	A1	11/2012	Jones-Albertus et al.
2013/0014815	A1	1/2013	Jones-Albertus et al.
2013/0118546	A1	5/2013	Jones-Albertus et al.
2013/0118566	A1	5/2013	Jones-Albertus et al.
2013/0220409	A1	8/2013	Jones-Albertus et al.

FOREIGN PATENT DOCUMENTS

JP	06061516		3/1994
JP	10012905		1/1998
WO	2010/151553	A1	12/2010
WO	2011/062886	A1	5/2011
WO	2011/123164	A1	10/2011
WO	2012/057874	A1	5/2012
WO	2012/115838	A1	8/2012
WO	2012/154455	A1	11/2012

OTHER PUBLICATIONS

Bertness et al., "29.5%-Efficient GaInP/GaAs Tandem Solar Cells," Applied Physics Letters, vol. 65, Aug. 22, 1994, pp. 989-991.

Bhuiyan et al., InGaN Solar Cells: Present State of the Art and Important Challenges, IEEE Journal of Photovoltaics, vol. 2, No. 3, Jul. 2012, pp. 246-293.

Cornfeld et al., "Evolution of a 2.05 eV AlGaInP Top Sub-cell for 5 and 6J-IMM Applications", Photovoltaic Specialists Conference (PVSC), 38th IEEE, Jun. 3, 2012, p. 2788-2791.

Cotal et al., "III-V multijunction solar cells for concentrating photovoltaics" pp. 174-192, www.rsc.org/ees, Energy and Environmental Science 2, (2009).

Denton et al., Vergard's Law, Physics Review A, The American Physical Society, 1991, vol. 43, No. 6, p. 3161-3164.

Ferguson et al., Nonradiative Recombination in 1.56 μm GaInNAsSb/GaNAs Quantum-Well Lasers, pp. 1-3, published online Dec. 8, 2009, Applied Physics Letters 95, 231104 (2009).

Fewster P.F., "X-Ray Scattering From Semiconductors" Second Edition, Imperial College Press, London, 2003, Ch. 1, pp. 1-22.

Friedman et al., "Analysis of the GaInP/GaAs/1-eV/Ge Cell and Related Structures for Terrestrial Concentration Application," pp. 856-859, Conference Record of the Twenty-ninth IEEE Photovoltaic Specialists Conference, New Orleans, LA., May 19-24, 2002.

Friedman et al., "Breakeven Criteria for the GaInNAs Junction in GaInP/GaAs/GaInNAs/Ge Four-junction Solar Cells", pp. 331-344, Progress in Photovoltaics: Research and Applications. (2002).

Friedman et al., "Analysis of Depletion-Region Collection in GaInNAs Solar Cells," pp. 691-694, Conference Record of the Thirty-first IEEE Photovoltaic Specialists Conference, Lake Buena Vista, Florida, Jan. 3-7, 2005.

(56) **References Cited**

OTHER PUBLICATIONS

Friedman et al., "1-eV Solar cells with GaInNAs active layer", Journal of Crystal Growth, vol. 195, 1998, p. 409-415.
Garcia et al., Analysis Of Tellurium As N-Type Dopant in GaInP: Doping, Diffusion, Memory Effect And Surfactant Properties, pp. 794-799, Journal of Crystal Growth 298 (2007).
Geelen et al., Epitaxial Lift-Off GaAs Solar Cell From A Reusable GaAs Substrate, pp. 162-171, Materials Science and Engineering B45 (1997).
Geisz et al., "Inverted GaInP / (In)GaAs / InGaAs triple-junction solar cells with low-stress metamorphic bottom junctions," Proceedings of the 33rd IEEE PVSC Photovoltaics Specialists Conference, (2008).
Green et al., Progress in Photovoltaics: Research and Applications 19 (2011) pp. 565-572.
Green et al., Progress in Photovoltaics: Research and Applications 20 (2012) pp. 12-20.
Green, "Third Generation Photovoltaics: Advanced Solar Energy Conversion," pp. 95-109, Springer Publishing, Berlin, Germany (2003).
Green, Do Built-in Fields Improve Solar Cell Performance? pp. 57-66, Progress in Photovoltaics: Research and Applications (2009), Published online in Wiley InterScience (www.interscience.wiley.com) on Oct. 1, 2008.
Gu et al., "Gas Source Growth and Doping Characteristics of A1InP on GaAs" Materials Science and Engineering B 131 (2006), pp. 49-53.
Harris Jr. et al., "Development of GainNAsSballoys: Growth, band structure, optical properties and applications," 2007, Physics Status Solidi(b), vol. 244, Issue 8, pp. 2707-2729, Jul. 6, 2007.
Hovel H.J., "Semiconductors and Semimetals", Academic Press, New York, 1975, Ch. 2, pp. 8-47.
Jackrel et al., "GaInNAsSb Solar Cells Grown by Molecular Beam Epitaxy," pp. 1-16, IEEE 4th World Conference on Photovoltaic Energy Conversion, Waikoloa, HI, 2006.
Jackrel et al., "GaInNAsSb Solar Cells Grown by Molecular Beam Epitaxy," 2006. Photovoltaic Energy Conversion, Conference Record of the 2006 IEEE 4th World Conference, vol. 1, p. 783-786, May 2006.
Jackrel et al., "Dilute nitride GainNAs and GainNAsSb solar cells by molecular beam epitaxy", pp. 1-8, Journal of Applied Physics 101 (114916), Jun. 14, 2007.
Janotti et. al., Mutual Passivation of Electrically Active and Isovalent Impurities in Dilute Nitrides, Physical Review Letters 100, 045505 (2008).
King et al., "High-Voltage, Low-Current GaInP/GaInP/GaAs/GaInNAs/Ge Solar Cells" Spectrolab Inc., 2002, pp. 852-855.
King et al., "40% Efficient Metamorphic GaInP/GaInAs/Ge Multijunction Solar Cells," J. of Applied Physics Letters, May 4, 2007.
Kudrawiec, "Contactless electroreflectance of GaInNAsSb/GaAs single quantum wells with indium content of 8%-32%", Jan. 2007, Journal of Applied Physics, vol. 101, pp. 013504-1-013504-9.
Kurtz et al., "Projected Performance of Three and Four-Junction Devices Using GaAs and GaInP," pp. 875-878, 26th IEEE Photovoltaics Specialists Conference, (1997).
Kurtz et al., "Understanding the potential and limitations of dilute nitride alloys for solar cells", Paper No. NREL/CP-520-38998, DOE Solar Energy Technologies Conference, Denver, CO, Nov. 7-10, 2005, 5 pages.
Law et al., "Future technology pathways of terrestrial III-V multijunction solar cells for concentrator photovoltaic systems", Solar Energy Materials & Solar Cells, 2010, 94, p. 1314-1318.
Merrill et al., Directions and Materials Challenges in High Performance Photovoltaics, Dec. 2007, JOM Energetic Thin Films, 59, 12, p. 26-30.
Miller et al., GaAs-AlGaAs tunnel junctions for multigap cascade solar cells, Journal of Applied Physics, vol. 53, No. 1, Jan. 1982, pp. 744-748.
Miyashita et al., Effect of Indium Composition on GaInNAsSb Solar Cells Grown by Atomic Hydrogen-Assisted Molecular Beam Epitaxy, pp. 632-635, 978-1-4244-2950@ 2009 IEEE.
Miyashita et al., "Improvement of GaInNAsSb films fabricated by atomic hydrogen-assisted molecular beam epitaxy", pp. 3249-3251, Journal of Crystal Growth 311, 2009.
Ng et al., 1EV GANXAS1-X-YSBY Material For Lattice-Matched III-V Solar Cell Implementation On GaAs and Ge, pp. 76-80, (2009).
Olson J.M. et al., "High-Efficiency III-V Multijunction Solar Cells" Handbook of Photovoltaic Science and Engineering, 1st ed.; Luque, A., Hegedus, S., Eds.; Wiley: New York, NY, USA, 2003; Chapter 9, pp. 359-411.
Patton et al., "Development of a High Efficiency Metamorphic Triple-junction 2.1 eV/1.6 eV/1.2 eV AlGaInP/InGaAsP/InGaAs Space Solar Cell", Conference Record of the IEEE Photovoltaic Specialists Conference, Institute of Electrical and Electronics Engineers Inc., May 19, 2002, vol. 29, p. 1027-1030.
Ptak et al., "Effects of Temperature, Nitrogen Ions and Antimony on Wide Depletion Width GaInNAs," pp. 955-959.J. Vac. Sci. Tech. B25(3), May/Jun. 2007 (published May 31, 2007).
Ptak et al., "Low-acceptor-Concentration GaInNAs grown by Molecular-beam Epitaxy for High-current p-i-n solar cell applications." J. of Applied Physics, 98.094501 (2005).
Ptak et al., "Defects in GaInNAs: What We've Learned so Far" National Renewable Energy Laboratory NREL/CP-520-33555, May 2003, 7 pages.
Sabnis et al., A new roadmap for space solar cells, Industry Photovoltaics, www.compoundsemiconductor.net/csc/features-details/19735471, Aug./Sep. 2012, 5 pages.
Solar Junction Inc, "Sharp Develops Solar Cell with Word's Highest Conversion Efficiency of 35.8%" Press Release, dated Oct. 22, 2009, 3 pages.
Volz et al., Optimization Of Annealing Conditions of (GaIn)(NAs) For Solar Cell Applications, pp. 2222-2228, Journal of Crystal Growth 310 (2008).
Volz et al., MOVPE growth of dilute nitride III/V semiconductors using all liquid metalorganic precursors, Journal of Crystal Growth 311 (2009), pp. 2418-2526.
E. Wesoff, "Update: Solar Junction breaking CPV efficiency records, raising $30M", Greentech Media, Apr. 15, 2011, 4 pages.
E. Wesoff, "CPV Roundup: SolFocus funding, 5MW order for Solar Junction, GreenVolts, Amonix", Greentech Media, May 22, 2012, 3 pages.
E. Wesoff, "Record 44 percent CPV efficiency from startup Solar Junction", Greentech Media, Oct. 15, 2012, 3 pages.
Weyers et al., "Red shift of photoluminescence and absorption in dilute GaAsN alloy layers", Japan Journal of Applied Physics, vol. 31, Issue 7A, 1992, p. L853-L855.
Wiemer et al., "43.5% Efficient Lattice Matched Solar Cells" Proc. SPIE 810804 (2011), 5 pages.
Wistey et al., Nitrogen Plasma Optimization For High-Quality Dilute Nitrides, pp. 229-233, Journal of Crystal Growth, available online on Feb. 1, 2005 at http://www.sciencedirect.com.
Wu et al., Band Anticrossing In Highly Mismatched III-V Semiconductor Alloys, pp. 860-869, Semiconductor Science and Technology 17 (2002).
Yamaguchi et al., "Multi-junction III-V solar cells: current status and future potential", in: Solar Energy, vol. 79, issue 1, Jul. 2005.
Yu et. al., Mutual Passivation Of Group IV Donors And Nitrogen In Diluted GaNxAs1-x Alloys, pp. 2844-2846, Applied Physics Letters, vol. 83, No. 14 (Oct. 6, 2003).
Yuen, "The role of antimony on properties of widely varying GaInNAsSb compositions", Journal of Applied Physics, May 2006, vol. 99, p. 093504-1 to 093804-8.
International Search Report and Written Opinion for PCT/US2008/008495, mailed on Apr. 6, 2009, 5 pages.
International Preliminary Report on Patentability for PCT/US2008/008495, mailed on Jan. 12, 2010, 5 pages.
International Search Report and Written Opinion for PCT/US2010/039534, mailed on Sep. 8, 2010, 8 pages.
International Search Report and Written Opinion for PCT/US2010/056800, mailed on Jan. 26, 2011, 8 pages.

(56) **References Cited**

OTHER PUBLICATIONS

International Search Report and Written Opinion for PCT/US2010/061635, mailed on Mar. 1, 2011, 7 pages.
International Search Report and Written Opinion for PCT/US2011/036486, mailed on Aug. 25, 2011, 12 pages.
International Preliminary Report on Patentability for PCT/US2010/056800, mailed on May 31, 2012, 6 pages.
International Search Report and Written Opinion for PCT/US2012/036020, mailed on Aug. 14, 2012, 11 pages.
International Search Report and Written Opinion for PCT/US2012/025307, mailed on Aug. 16, 2012, 13 pages.
International Search Report and Written Opinion for PCT/US2013/033567, mailed on Mar. 4, 2014, 12 pages.
Amendment, Affidavits under 37 C.F.R. §132, and Information Disclosure Statement filed Nov. 2013 for U.S. Appl. No. 13/739,989, 51 pages.
Non-Final Office Action dated Feb. 20, 2014, for U.S. Appl. No. 13/678,389, 13 pages.
Non-Final Office Action dated Dec. 31, 2013, for U.S. Appl. No. 13/370,500, 7 pages.
Non-Final Office Action dated Dec. 14, 2012, for U.S. Appl. No. 13/618,496, 16 pages.
Non-Final Office Action dated Jun. 10, 2010, for U.S. Appl. No. 12/217,818, 15 pages.
Final Office Action dated Jan. 1, 2011, for U.S. Appl. No. 12/217,818, 15 pages.
Non-Final Office Action dated Oct. 5, 2012, for U.S. Appl. No. 12/944,439, 15 pages.
Final Office Action dated May 29, 2013, for U.S. Appl. No. 12/944,439, 11 pages.
Non-Final Office Action dated Aug. 13, 2014, for U.S. Appl. No. 12/944,439, 11 pages.
Non-Final Office Action dated Oct. 24, 2012, for U.S. Appl. No. 12/749,076, 17 pages.
Final Office Action dated Feb. 6, 2013, for U.S. Appl. No. 13/618,496, 8 pages.
Non-Final Office Action dated Feb. 13, 2013, for U.S. Appl. No. 12/819,534, 8 pages.
Final Office Action dated Sep. 9, 2013, for U.S. Appl. No. 12/819,534, 13 pages.
Non-Final Office Action dated Feb. 15, 2013, for U.S. Appl. No. 12/914,710, 14 pages.
Final Office Action dated Sep. 6, 2013, for U.S. Appl. No. 12/914,710, 17 pages.
Notice of Allowance dated Mar. 22, 2013, for U.S. Appl. No. 13/618,496, 8 pages.
Non-Final Office Action dated Feb. 15, 2013, for U.S. Appl. No. 13/708,763, 23 pages.
Notice of Allowance dated Feb. 20, 2014, for U.S. Appl. No. 13/708,763, 9 pages.
Non-Final Office Action dated Feb. 25, 2013, for U.S. Appl. No. 13/708,791, 16 pages.
Final Office Action dated Oct. 1, 2013, for U.S. Appl. No. 13/708,791, 15 pages.
Final Office Action dated Feb. 26, 2014, for U.S. Appl. No. 13/739,989, 16 pages.
Non-Final Office Action dated May 24, 2013, for U.S. Appl. No. 13/739,989, 7 pages.
Non-Final Office Action dated Nov. 8, 2012, for U.S. Appl. No. 13/104,913, 12 pages.
Final Office Action dated Oct. 2, 2013, for U.S. Appl. No. 13/104,913, 12 pages.
Notice of Allowance dated Feb. 21, 2014, for U.S. Appl. No. 13/104,913, 8 pages.
Notice of Allowance for U.S. Appl. No. 13/708,791, mailed on Oct. 31, 2014, 8 pages.
Notice of Allowance for U.S. Appl. No. 13/370,500, mailed on Sep. 22, 2014, 10 pages.
Notice of Allowance for U.S. Appl. No. 13/739,989, mailed on Sep. 30, 2014, 9 pages.
Non-Final Office Action dated Mar. 21, 2014, for U.S. Appl. No. 13/442,146, 6 pages.
Declaration Under 37 C.F.R. § 1.132 of Homan Yuen filed for U.S. Appl. No. 13/739,989 on Nov. 15, 2013, pp. 1-10.
Declaration Under 37 C.F.R. § 1.132 of Jerry Olson filed for U.S. Appl. No. 13/739,989 on Nov. 15, 2013, pp. 1-5.
Declaration Under 37 C.F.R. § 1.132 of Minjoo Lee filed for U.S. Appl. No. 13/739,989 on Nov. 15, 2013, pp. 1-6.
Japanese Application No. 2012-517662, Office Action mailed on Apr. 30, 2013, 5 pages. (English translation).
Japanese Application No. 2013-502560, Office Action mailed on May 7, 2014, 5 pages. (English translation).
Japanese Application No. 2013-536607, Office Action mailed on Mar. 18, 2014, 6 pages. (English translation).

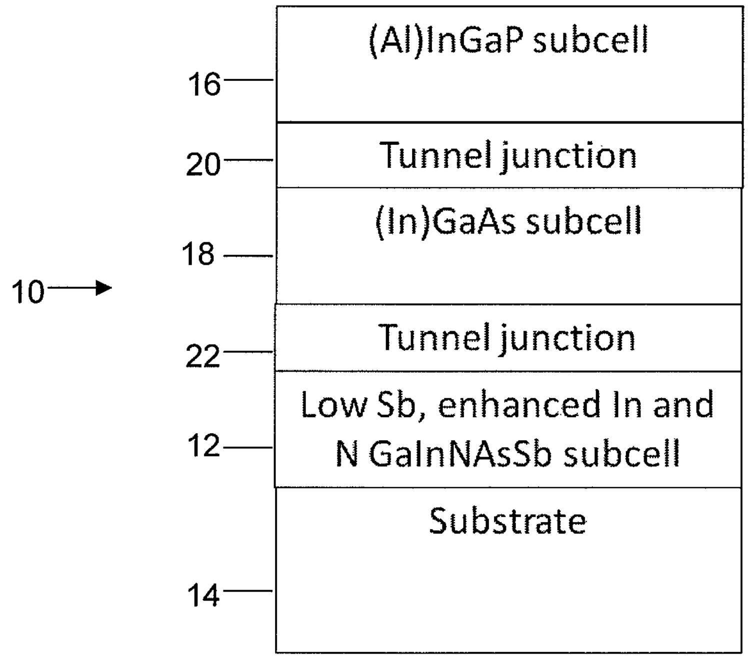

(Al)InGaP subcell
16
Tunnel junction
20
(In)GaAs subcell
18
10
Tunnel junction
22
Low Sb, enhanced In and N GaInNAsSb subcell
12
Substrate
14

FIG. 1A

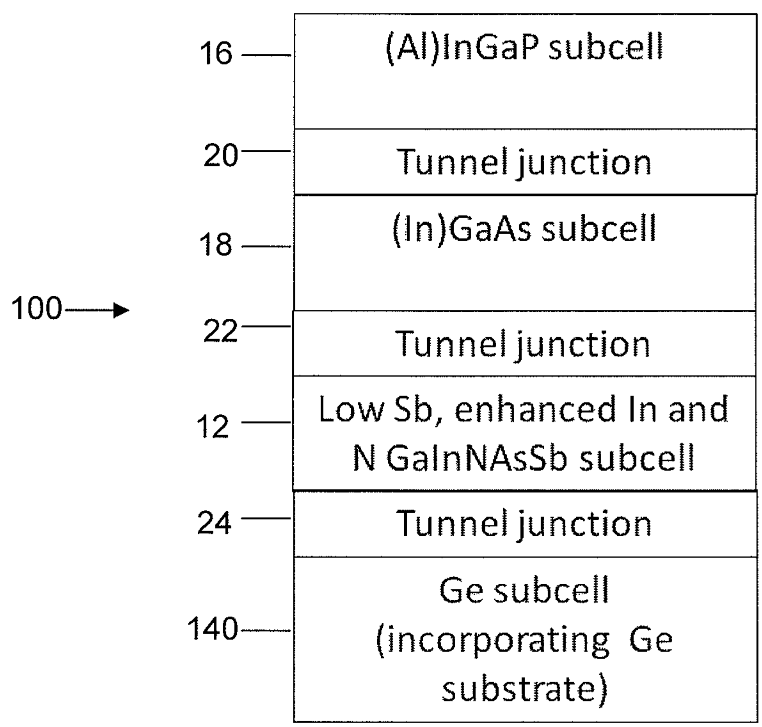

(Al)InGaP subcell
16
Tunnel junction
20
(In)GaAs subcell
18
100
Tunnel junction
22
Low Sb, enhanced In and N GaInNAsSb subcell
12
Tunnel junction
24
Ge subcell (incorporating Ge substrate)
140

FIG. 1B

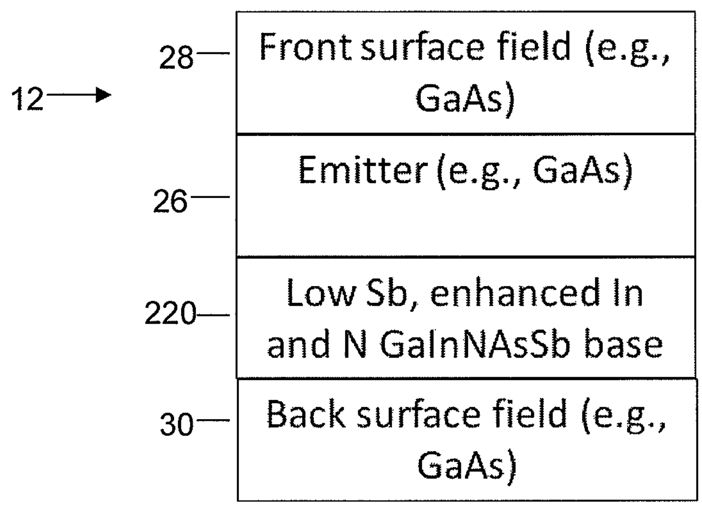

28
12
Front surface field (e.g., GaAs)
26
Emitter (e.g., GaAs)
220
Low Sb, enhanced In and N GaInNAsSb base
30
Back surface field (e.g., GaAs)

FIG. 2A

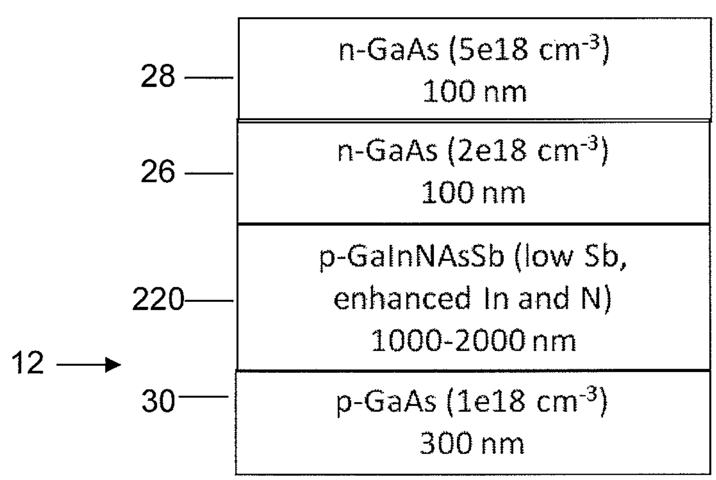

28
n-GaAs (5e18 cm-3) 100 nm
26
n-GaAs (2e18 cm-3) 100 nm
220
p-GaInNAsSb (low Sb, enhanced In and N) 1000-2000 nm
12
30
p-GaAs (1e18 cm-3) 300 nm

FIG. 2B

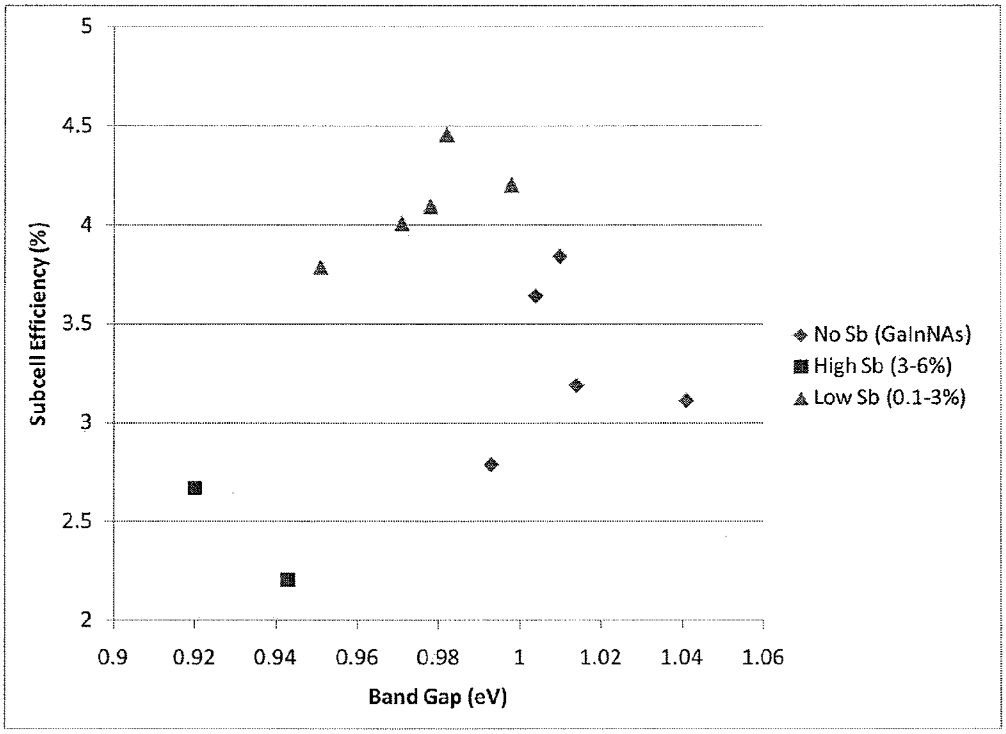

Subcell Efficiency (%)
5
4.5
4
3.5
3
2.5
2
0.9
0.92
0.94
0.96
0.98
1
1.02
1.04
1.06
Band Gap (eV)
No Sb (GaInNAs)
High Sb (3-6%)
Low Sb (0.1-3%)

FIG. 3

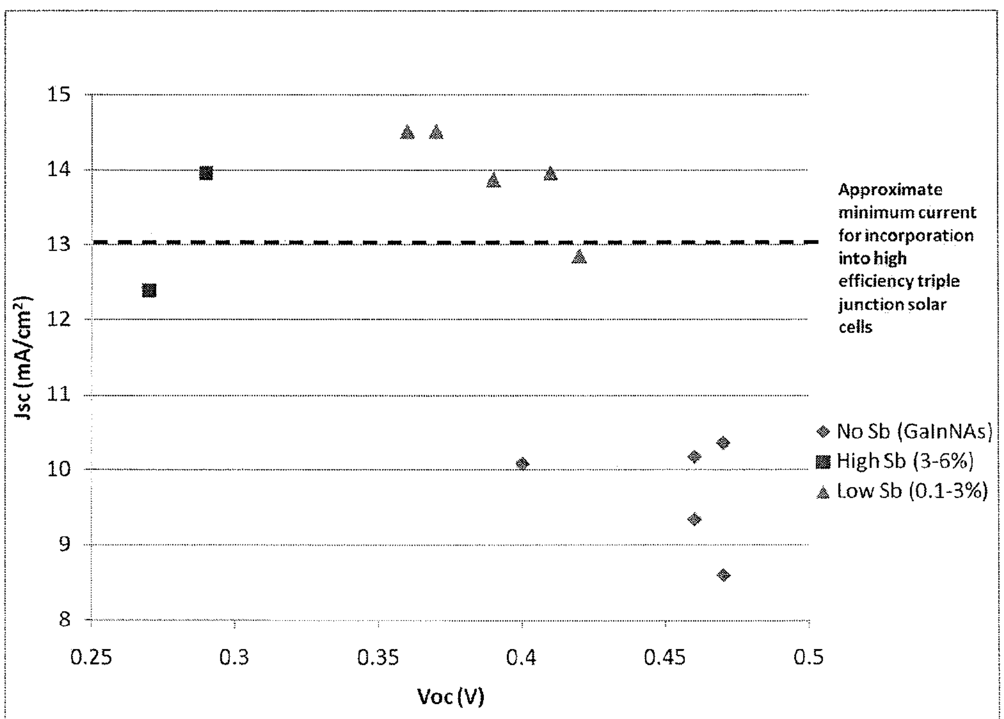

Jsc (mA/cm²)
15
14
13
12
11
10
9
8
0.25
0.3
0.35
0.4
0.45
0.5
Voc (V)
Approximate minimum current for incorporation into high efficiency triple junction solar cells
No Sb (GaInNAs)
High Sb (3-6%)
Low Sb (0.1-3%)

FIG. 4

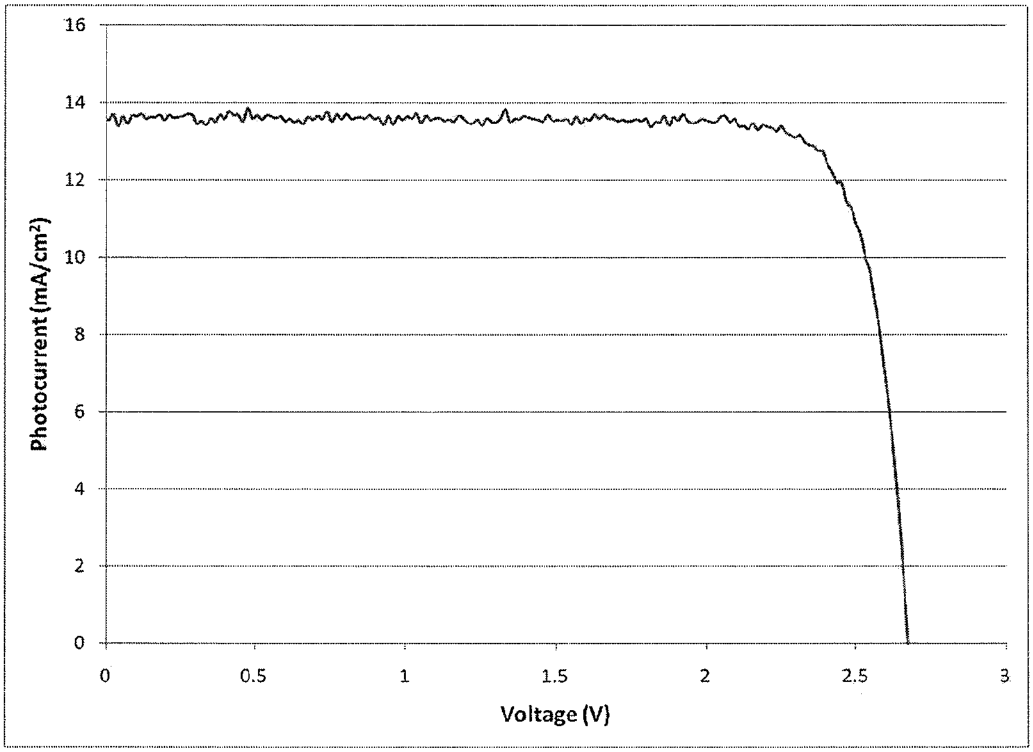

16
14
12
10
8
6
4
2
0
Photocurrent (mA/cm²)
0
0.5
1
1.5
2
2.5
3
Voltage (V)

FIG. 5

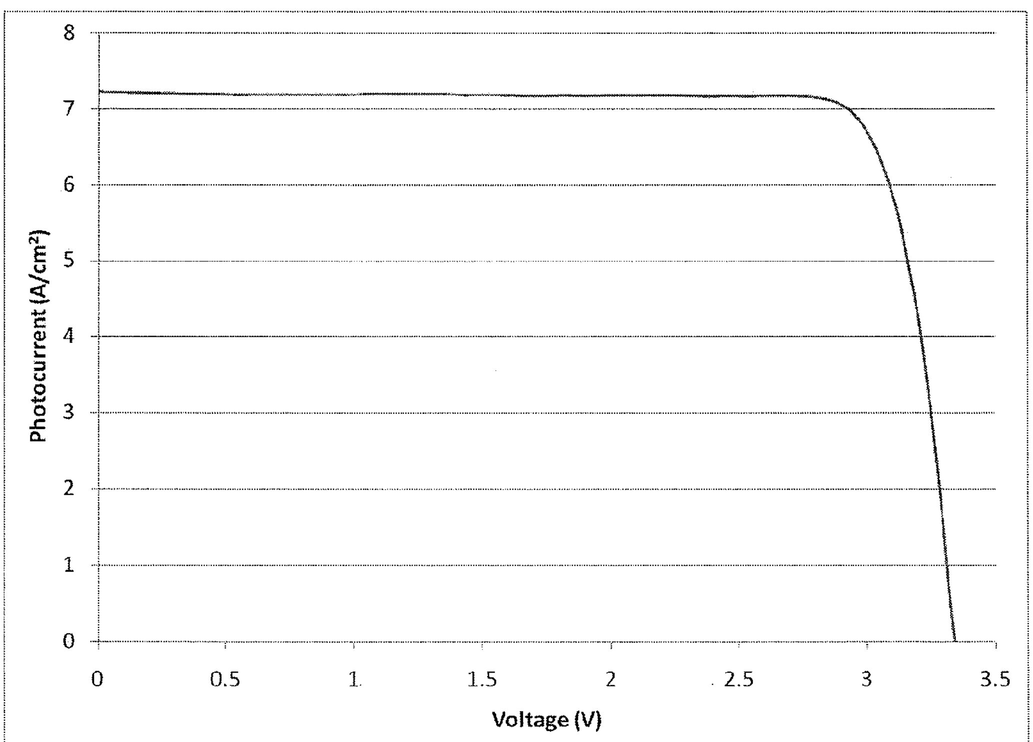

8
7
6
5
4
3
2
1
0
Photocurrent (A/cm²)
0
0.5
1
1.5
2
2.5
3
3.5
Voltage (V)

FIG. 6

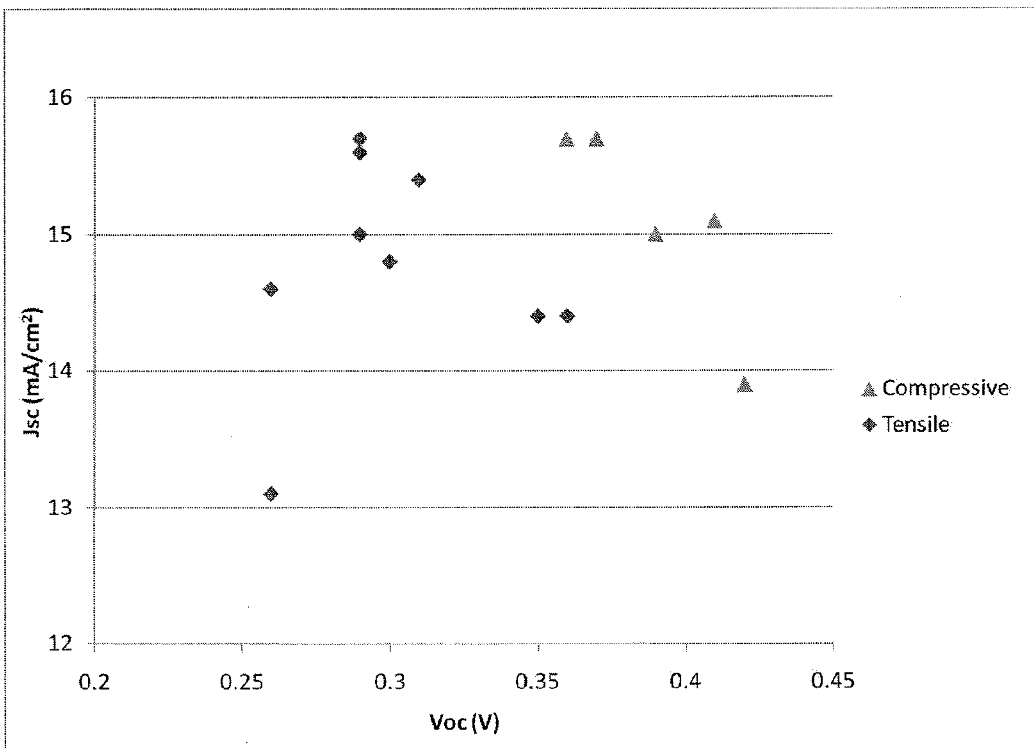

16
15
14
13
12
Jsc (mA/cm²)
0.2
0.25
0.3
0.35
0.4
0.45
Voc (V)
Compressive
Tensile

FIG. 7

LATTICE MATCHABLE ALLOY FOR SOLAR CELLS

This application is a continuation of U.S. application Ser. No. 14/597,621, filed on Jan. 15, 2015, which is a continuation of U.S. application Ser. No. 14/512,224, now allowed, filed on Oct. 10, 2014, which is a continuation of U.S. application Ser. No. 13/739,989, filed on Jan. 11, 2013, issued as U.S. Pat. No. 8,912,433, which is a divisional of U.S. application Ser. No. 12/749,076, filed on Mar. 29, 2010, each of which is incorporated by reference herein in its entirety.

BACKGROUND OF THE INVENTION

The present invention relates to multijunction solar cells, and in particular to high efficiency solar cells comprised of III-V semiconductor alloys.

Multijunction solar cells made primarily of III-V semiconductor alloys are known to produce solar cell efficiencies exceeding efficiencies of other types of photovoltaic materials. Such alloys are combinations of elements drawn from columns III and V of the standard Periodic Table, identified hereinafter by their standard chemical symbols, names and abbreviation. (Those of skill in the art can identify their class of semiconductor properties by class without specific reference to their column.) The high efficiencies of these solar cells make them attractive for terrestrial concentrating photovoltaic systems and systems designed to operate in outer space. Multijunction solar cells with efficiencies above 40% under concentrations equivalent to several hundred suns have been reported. The known highest efficiency devices have three subcells with each subcell consisting of a functional p-n junction and other layers, such as front and back surface field layers. These subcells are connected through tunnel junctions, and the dominant layers are either lattice matched to the underlying substrate or are grown over metamorphic layers. Lattice-matched devices and designs are desirable because they have proven reliability and because they use less semiconductor material than metamorphic solar cells, which require relatively thick buffer layers to accommodate differences in the lattice constants of the various materials. As set forth more fully in U.S. patent application Ser. No. 12/217,818, entitled "GaInNAsSb Solar Cells Grown by Molecular Beam Epitaxy," which application is incorporated herein by reference, a layer made of GaInNAsSb material to create a third junction having a band gap of approximately 1.0 eV offers a promising approach to improving the efficiency of multijunction cells. Improvements are nevertheless to be considered on the cell described in that application.

The known highest efficiency, lattice-matched solar cells typically include a monolithic stack of three functional p-n junctions, or subcells, grown epitaxially on a germanium (Ge) substrate. The top subcell has been made of (Al)GaInP, the middle one of (In)GaAs, and the bottom junction included the Ge substrate. (The foregoing nomenclature for a III-V alloy, wherein a constituent element is shown parenthetically, denotes a condition of variability in which that particular element can be zero.) This structure is not optimal for efficiency, in that the bottom junction can generate roughly twice the short circuit current of the upper two junctions, as reported by J. F. Geisz et al., "Inverted GaInP/(In)GaAs/InGaAs triple junction solar cells with low-stress metamorphic bottom junctions," *Proceedings of the* 33rd *IEEE PVSC Photovoltaics Specialists Conference,* 2008. This extra current capability is wasted, since the net current must be uniform through the entire stack, a design feature known as current matching.

In the disclosure of above noted U.S. patent application Ser. No. 12/217,818, it was shown that a material that is substantially lattice matched to Ge or GaAs with a band gap near 1.0 eV might be used to create a triple junction solar cell with efficiencies higher than the structure described above by replacing the bottom Ge junction with a junction made of a different material that produces a higher voltage.

In addition, it has been suggested that the use of this 1 eV material might be considered as a fourth junction to take advantage of the entire portion of the spectrum lying between 0.7 eV (the band gap for germanium) and 1.1 eV (the upper end of the range of bandgaps for the ~1 eV layer). See for example, S. R. Kurtz, D. Myers, and J. M. Olson, "Projected Performance of Three and Four-Junction Devices Using GaAs and GaInP," *26th IEEE Photovoltaics Specialists Conference,* 1997, pp. 875-878. $Ga_{1-x}In_xN_yAs_{1-y}$ has been identified as such a 1 eV material, but currents high enough to match the other subcells have not been achieved, see, e.g., A. J. Ptak et al., *Journal of Applied Physics* 98 (2005) 094501. This has been attributed to low minority carrier diffusion lengths that prevent effective photocarrier collection. Solar subcell design composed of gallium, indium, nitrogen, arsenic and various concentrations of antimony (GaInNAsSb) has been investigated with the reported outcome that antimony is helpful in decreasing surface roughness and allowing growth at higher substrate temperatures where annealing is not necessary, but the investigators reported that antimony, even in small concentrations is critical to be avoided as detrimental to adequate device performance. See Ptak et al., "Effects of temperature, nitrogen ion, and antimony on wide depletion width GaInNAs," *Journal of Vacuum Science Technology* B 25(3) May/June 2007 pp. 955-959. Devices reported in that paper have short circuit currents far too low for integration into multijunction solar cells. Nevertheless, it is known that $Ga_{1-x}In_xN_yAs_{1-y-z}Sb_z$ with $0.05 \leq x \leq 0.07$, $0.01 \leq y \leq 0.02$ and $0.02 \leq z \leq 0.06$ can be used to produce a lattice-matched material with a band gap of approximately 1 eV that can provide sufficient current for integration into a multijunction solar cell. However, the voltages generated by subcells containing this material have not exceeded 0.30 V under 1 sun of illumination. See D. B. Jackrel et al., *Journal of Applied Physics* 101 (114916) 2007. Thus, a triple-junction solar cell with this material as the bottom subcell has been expected to be only a small improvement upon an analogous triple junction solar cell with a bottom subcell of Ge, which produces an open circuit voltage of approximately 0.25 V. See H. Cotal et al., *Energy and Environmental Science* 2 (174) 2009. What is needed is a material that is lattice-matched to Ge and GaAs with a band gap near 1 eV that produces an open circuit voltage greater than 0.30 V and sufficient current to match (Al)InGaP and (In)GaAs subcells. Such a material would also be advantageous as a subcell in high efficiency solar cells with 4 or more junctions.

SUMMARY OF THE INVENTION

According to the invention, an alloy composition is provided that has a bandgap of at least 0.9 eV, namely, $Ga_{1-x}In_xN_yAs_{1-y-z}Sb_z$ with a low antimony (Sb) content and with enhanced indium (In) content and enhanced nitrogen (N) content as compared with known alloys of GaInNAsSb, achieving substantial lattice matching to GaAs and Ge substrates and providing both high short circuit currents and high open circuit voltages in GaInNAsSb subcells suitable for use in multijunction solar cells. The composition ranges for $Ga_{1-x}In_xN_yAs_{1-y-z}Sb_z$ are $0.07 \leq x \leq 0.18$, $0.025 \leq y \leq 0.04$ and

$0.001 \le z \le 0.03$. These composition ranges employ greater fractions of In and N in GaInNAsSb than previously taught and allow the creation of subcells with bandgaps that are design-tunable in the range of 0.9-1.1 eV, which is the range of interest for GaInNAsSb subcells. This composition range alloy will hereinafter be denoted "low-antimony, enhanced indium-and-nitrogen GaInNAsSb" alloy. Subcells of such an alloy can be grown by molecular beam epitaxy (MBE) and should be able to be grown by metallorganic chemical vapor deposition (MOCVD), using techniques known to one skilled in the art.

The invention described herein reflects a further refinement of work described in U.S. patent application Ser. No. 12/217,818, including the discovery and identification of specific ranges of elements, i.e., a specific alloy mix of the various elements in GaInNAsSb that improve significantly the performance of the disclosed solar cells.

The invention will be better understood by reference to the following detailed description in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1**A is a schematic cross-section of a three junction solar cell incorporating the invention.

FIG. **1**B is a schematic cross-section of a four junction solar cell incorporating the invention.

FIG. **2**A is a schematic cross-section of a GaInNAsSb subcell according to the invention.

FIG. **2**B is a detailed schematic cross-section illustrating an example GaInNAsSb subcell.

FIG. **3** is a graph showing the efficiency versus band gap energy of subcells formed from different alloy materials, for comparison.

FIG. **4** is a plot showing the short circuit current (J_{sc}) and open circuit voltage (V_{oc}) of subcells formed from different alloy materials, for comparison.

FIG. **5** is a graph showing the photocurrent as a function of voltage for a triple junction solar cell incorporating a subcell according to the invention, under 1-sun AM1.5D illumination.

FIG. **6** is a graph showing the photocurrent as a function of voltage for a triple junction solar cell incorporating a subcell according to the invention, under AM1.5D illumination equivalent to 523 suns.

FIG. **7** is a graph of the short circuit current (J_{sc}) and open circuit voltage (V_{oc}) of low Sb, enhanced In and N GaInNAsSb subcells distinguished by the strain imparted to the film by the substrate.

DETAILED DESCRIPTION OF THE INVENTION

FIG. **1**A is a schematic cross-section showing an example of a triple junction solar cell **10** according to the invention consisting essentially of a low Sb, enhanced In and N GaInNAsSb subcell **12** adjacent the Ge, GaAs or otherwise compatible substrate **14** with a top subcell **16** of (Al)InGaP and a middle subcell **18** using (In)GaAs. Tunnel junction **20** is between subcells **16** and **18**, while tunnel junction **22** is between subcells **18** and **12**. Each of the subcells **12**, **16**, **18** comprises several associated layers, including front and back surface fields, an emitter and a base. The named subcell material (e.g., (In)GaAs) forms the base layer, and may or may not form the other layers.

Low Sb, enhanced In and N GaInNAsSb subcells may also be incorporated into multijunction solar cells with four or more junctions without departing from the spirit and scope of the invention. FIG. **1**B shows one such four junction solar cell **100** with a specific low Sb, enhanced In and N GaInNAsSb subcell **12** as the third junction, and with a top subcell **16** of (Al)InGaP, a second subcell **18** of (In)GaAs and a bottom subcell **140** of Ge, which is also incorporated into a germanium (Ge) substrate. Each of the subcells **16**, **18**, **12**, **140** is separated by respective tunnel junctions **20**, **22**, **24**, and each of the subcells **16**, **18**, **12**, **140** may comprise several associated layers, including optional front and back surface fields, an emitter and a base. The named subcell material (e.g., (In)GaAs) forms the base layer, and may or may not form the other layers.

By way of further illustration, FIG. **2**A is a schematic cross-section in greater detail of a GaInNAsSb subcell **12**, according to the invention. The low Sb, enhanced In and N GaInNAsSb subcell **12** is therefore characterized by its use of low Sb, enhanced In and N GaInNAsSb as the base layer **220** in the subcell **12**. Other components of the GaInNAsSb subcell **12**, including an emitter **26**, an optional front surface field **28** and back surface field **30**, are preferably III-V alloys, including by way of example GaInNAs(Sb), (In)(Al)GaAs, (Al)InGaP or Ge. The low Sb, enhanced In and N GaInNAsSb base **220** may either be p-type or n-type, with an emitter **26** of the opposite type.

To determine the effect of Sb on enhanced In and N GaInNAsSb subcell performance, various subcells of the type (12) of the structure shown in FIG. **2**B were investigated. FIG. **2**B is a representative example of the more general structure **12** in FIG. **2**A. Base layers **220** with no Sb, low Sb ($0.001 \le z \le 0.03$) and high Sb ($0.03 < z < 0.06$) were grown by molecular beam epitaxy and were substantially lattice-matched to a GaAs substrate (not shown). These alloy compositions were verified by secondary ion mass spectroscopy. The subcells **12** were subjected to a thermal anneal, processed with generally known solar cell processing, and then measured under the AM1.5D spectrum (1 sun) below a filter that blocked all light above the GaAs band gap. This filter was appropriate because a GaInNAsSb subcell **12** is typically beneath an (In)GaAs subcell in a multijunction stack (e.g., FIGS. **1**A and **1**B), and thus light of higher energies will not reach the subcell **12**.

FIG. **3** shows the efficiencies produced by the subcells **12** grown with different fractions of Sb as a function of their band gaps. The indium and nitrogen concentrations were each in the 0.07 to 0.18 and 0.025 to 0.04 ranges, respectively. It can be seen that the low Sb, enhanced In and N GaInNAsSb subcells (represented by triangles) have consistently higher subcell efficiencies than the other two candidates (represented by diamonds and squares). This is due to the combination of high voltage and high current capabilities in the low Sb, enhanced In and N GaInNAsSb devices. (See FIG. **4**). As can be seen in FIG. **4**, both the low and high concentration Sb devices have sufficient short-circuit current to match high efficiency (Al)InGaP subcells and (In)GaAs subcells (>13 mA/cm^2 under the filtered AM1.5D spectrum), and thus they may be used in typical three junction or four-junction solar cells **10**, **100** without reducing the total current through the entire cell. This current-matching is essential for high efficiency. The devices without Sb have relatively high subcell efficiencies due to their high open circuit voltages, but their short circuit currents are too low for high efficiency multijunction solar cells, as is shown in FIG. **4**.

FIG. **4** also confirms that Sb has a deleterious effect on voltage, as previously reported for other alloy compositions. However, in contrast to what has been previously reported for other alloy compositions, the addition of antimony does NOT decrease the short circuit current. The low Sb-type subcells have roughly 100 mV higher open-circuit voltages than the high Sb-type subcells. To illustrate the effect of this improvement, a triple junction solar cell **10** with an open circuit voltage of 3.1 V is found to have 3.3% higher relative efficiency compared to an otherwise identical cell with an open circuit voltage of 3.0 V. Thus, the inclusion of Sb in GaInNAs (Sb) solar cells is necessary to produce sufficient current for a high efficiency solar cell, but only by using low Sb (0.1-3%) can both high voltages and high currents be achieved.

Compressive strain improves the open circuit voltage of low Sb, enhanced In and N GaInNAsSb subcells **10**, **100**. More specifically, low Sb, enhanced In and N GaInNAsSb layers **220** that have a lattice constant larger than that of a GaAs or Ge substrate when fully relaxed (≤0.5% larger), and are thus under compressive strain when grown pseudomorphically on those substrates. They also give better device performance than layers with a smaller, fully relaxed lattice constant (under tensile strain).

FIG. **7** shows the short circuit current and open circuit voltage of low Sb, enhanced In and N GaInNAsSb subcells grown on GaAs substrates under compressive strain (triangles) and tensile strain (diamonds). It can be seen that the subcells under compressive strain have consistently higher open circuit voltages than those under tensile strain.

Low Sb, enhanced In and N, compressively-strained GaInNAsSb subcells have been successfully integrated into high efficiency multijunction solar cells. FIG. **5** shows a current-voltage curve of a triple junction solar cell of the structure in FIG. **1**A under AM1.5D illumination equivalent to 1 sun. The efficiency of this device is 30.5%. FIG. **6** shows the current-voltage curve of the triple junction solar cell operated under a concentration equivalent to 523 suns, with an efficiency of 39.2%.

The invention has been explained with reference to specific embodiments. Other embodiments will be evident to those of ordinary skill in the art. It is therefore not intended for the invention to be limited, except as indicated by the appended claims.

What is claimed is:

1. A semiconductor alloy composition, wherein the semiconductor alloy composition is $Ga_{1-x}In_xN_yAs_{1-y-z}Sb_z$, wherein,

the content values for x, y, and z are within composition ranges as follows: $0.07 \leq x \leq 0.18$, $0.025 \leq y \leq 0.04$ and $0.001 \leq z \leq 0.03$;

the content levels are selected such that the semiconductor alloy composition exhibits a bandgap from 0.9 eV to 1.1 eV; and a short circuit current density Jsc greater than 13 mA/cm^2 and an open circuit voltage Voc greater than 0.3 V when illuminated with a filtered 1 sun AM1.5D spectrum in which all light having an energy greater than the bandgap of GaAs is blocked.

2. The semiconductor alloy composition of claim **1**, wherein the semiconductor alloy composition is characterized by a thickness from 1 μm to 2 μm.

3. The semiconductor alloy composition of claim **1**, wherein the semiconductor alloy composition is characterized by a thickness greater than 1 μm.

4. The semiconductor alloy composition of claim **1**, wherein the semiconductor alloy composition is substantially lattice matched to GaAs.

5. The semiconductor alloy composition of claim **1**, wherein the semiconductor alloy composition is substantially lattice matched to Ge.

6. The semiconductor alloy composition of claim **1**, wherein the semiconductor alloy composition is n-doped.

7. The semiconductor alloy composition of claim **1**, wherein the semiconductor alloy composition is p-doped.

8. The semiconductor alloy composition of claim **1**, wherein the semiconductor alloy composition is in the form of a layer of semiconductor material.

9. The semiconductor alloy composition of claim **1**, wherein the content values are selected such that the semiconductor alloy composition is lattice matched to GaAs or Ge.

* * * * *